PATENT ABSTRACTS OF JAPAN

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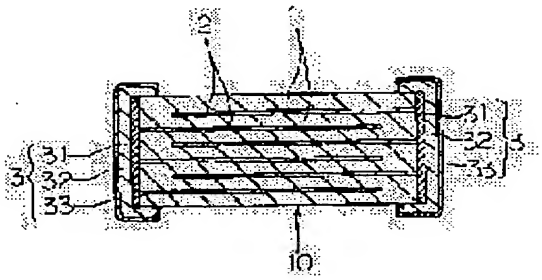
(54) LAMINATED CERAMIC CAPACITOR

(57)Abstract:
PROBLEM TO BE SOLVED: To improve the insulation resistance of a dielectric ceramic layer and, at the same time, to stably electrically connect internal electrodes composed mainly of Ni layers to external electrodes by preventing the corrosion of the internal electrode layers through a plating solution.
SOLUTION: A laminated ceramic capacitor is provided with a laminated body 10, formed by alternately laminating dielectric ceramic layers 1 and internal electrode layers 2, composed mainly of Ni upon another and external electrodes 3 formed on the end faces of the laminated body. Each external electrode 3 is composed of a baser conductor film 31 connected to half of the internal electrode layers 2, a thermosetting conducive resin film 32 formed on the surface of the conductor film 31, and a surface plated layer 33 formed on the surface of the resin film 32. At the same time, the conductor film 31 is composed mainly of Cu and is set to a thickness of 5-30 μm.



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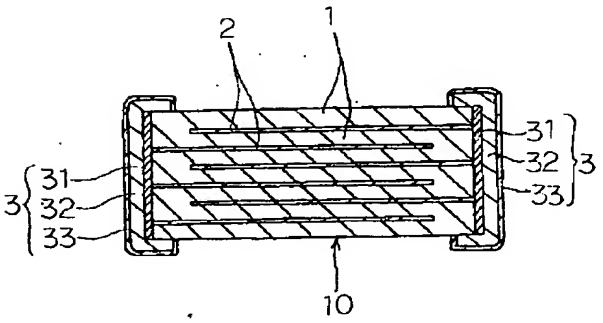
(54)【発明の名称】　積層セラミックコンデンサ

(57)【要約】

【課題】誘電体セラミック層の絶縁抵抗を向上できるとともに、メッキ液による内部電極層の腐食を防止して、Ｎｉ主成分からなる内部電極層と外部電極との安定した電気的な接続を達成できる積層セラミックコンデンサを提供する。

【解決手段】誘電体セラミック層１とＮｉを主成分とする内部電極層２とを交互に積層した積層体１０と、該積層体１０の端面に形成された外部電極３とを具備した積層セラミックコンデンサであって、外部電極３を、内部電極層２と接続する下地導体膜３１と、この下地導体膜３１表面に形成された熱硬化性導電性樹脂膜３２と、この熱硬化性導電性樹脂膜３２の表面に形成された表面メッキ層３３とから構成するとともに、下地導体膜３１がＣｕを主成分とし、かつその厚みが５～３０μｍであることを特徴とする。



1

【特許請求の範囲】
【請求項１】誘電体セラミック層とＮｉを主成分とする内部電極層とを交互に積層した積層体と、該積層体の端面に形成された外部電極とを具備した積層セラミックコンデンサであって、前記外部電極を、前記内部電極層と接続する下地導体膜と、この下地導体膜表面に形成された熱硬化性導電性樹脂膜と、この熱硬化性導電性樹脂膜の表面に形成された表面メッキ層とから構成するとともに、前記下地導体膜がＣｕを主成分とし、かつその厚みが５～３０μｍであることを特徴とする積層セラミックコンデンサ。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は、積層セラミックコンデンサに関し、特に、誘電体セラミック層とＮｉを主成分とする内部電極層とを交互に積層した積層体と、この積層体の端面に形成された外部電極とを具備した積層セラミックコンデンサに関する。
【０００２】
【従来技術】近年、積層セラミックコンデンサの内部電極層としてＡｇ－Ｐｄ合金が使用されているが、最近の低コスト化に対応するために、内部電極層にＮｉ、Ｃｕなどの卑金属材料が使用されるようになっている。このＮｉ、Ｃｕなどの卑金属は酸化され易い材料であるため、特に内部電極層の形成工程にあたり、また、形成した後の工程、例えば外部電極の形成工程で、内部電極層の酸化を防止することが重要である。
【０００３】例えば、内部電極層の焼成工程、即ち、誘電体セラミック層と内部電極層とが交互に積層された積層成形体の焼成工程や、その後の外部電極の形成工程は、低酸素濃度（10^{-8}～10^{-12} ａｔｍ）雰囲気で焼成していた。
【０００４】内部電極層材料としてＮｉ、Ｃｕなどの卑金属材料を用いた積層セラミックコンデンサの外部電極として、従来、特公平８－４０５５号公報には、銅の焼き付け電極からなるものが開示されており、このような積層セラミックコンデンサにおける銅の焼き付け電極は、銅粉末５５～８０重量％と、ガラスフリット５～２０重量％と、有機ビヒクル１０～３０重量％とからなる銅ペーストを塗布し、弱還元雰囲気中８００℃、３０分の条件で焼き付けて形成されていた。このような銅の焼き付け電極は、通常剥離等を防止するために６０～１００μｍ程度の厚みとされていた。
【０００５】
【発明が解決しようとする課題】しかしながら、銅の焼き付け電極の厚みが６０～１００μｍと厚いため、脱バインダー処理しても電極中の炭素を完全に飛散できずに残存し、内部電極層の焼成工程や外部電極の形成工程で、上述のような低酸素濃度の焼成処理を行うと誘電体セラミック層が還元され、誘電体セラミック材料の特性

2

が変化してしまい、特に、コンデンサとしての絶縁抵抗値が低下してしまうという致命的な問題を誘発してしまう。
【０００６】絶縁抵抗値が低下してしまった積層セラミックコンデンサにおいては、絶縁抵抗値を回復するために、例えば、高い酸素濃度雰囲気で熱処理して酸素を補うことが考えられる。例えば、積層体焼結後の熱処理工程である外部電極の焼き付け工程において高い酸素分圧で熱処理を行うと、外部電極を通して内部電極層が酸化され、内部電極層と外部電極との導通がとれず、静電容量がバラツクという問題があった。結局、外部電極は低い酸素分圧で焼き付けせざるを得ず、誘電体セラミック層の絶縁抵抗値の改善は困難であった。
【０００７】このような誘電体セラミック層の絶縁抵抗の低下を防止するために、銅の焼き付け電極を薄くすることが考えられる。しかしながら、銅の焼き付け電極の表面には、一般に、ハンダとの濡れ性を向上し、外部電極のハンダ食われを防止するためにメッキ処理が施されるが、このメッキ液が銅の焼き付け電極を透過し、Ｎｉを主成分とする内部電極層を腐食させ、外部電極との電気的な接続が不安定となったり、また内部電極層が腐食して剥離しクラックやデラミネーションが発生するという問題があった。
【０００８】また、誘電体セラミック層の絶縁抵抗の低下を防止するために銅ペーストを８００℃以下の低温で焼成しても良いが、この場合には銅の焼き付け電極の緻密化が図れず、メッキ後に内部電極層が腐食し、上記と同様の問題があった。
【０００９】本発明は上述の課題に鑑みて案出されたものであり、その目的は、誘電体セラミック層の絶縁抵抗を向上できるとともに、メッキ液による内部電極層の腐食を防止して、Ｎｉ主成分からなる内部電極層と外部電極との安定した電気的な接続を達成できる積層セラミックコンデンサを提供することである。
【００１０】
【課題を解決しようとする手段】本発明の積層セラミックコンデンサは、誘電体セラミック層とＮｉを主成分とする内部電極層とを交互に積層した積層体と、該積層体の端面に形成された外部電極とを具備した積層セラミックコンデンサであって、前記外部電極を、前記内部電極層と接続する下地導体膜と、この下地導体膜表面に形成された熱硬化性導電性樹脂膜と、この熱硬化性導電性樹脂膜の表面に形成された表面メッキ層とから構成するとともに、前記下地導体膜がＣｕを主成分とし、かつその厚みが５～３０μｍであることを特徴とする。
【００１１】
【作用】本発明によれば、Ｃｕを主成分とする下地導体膜の厚みを５～３０μｍとし、従来よりも薄くしたため、脱バインダー処理において有機溶媒を完全に飛散させることができ、焼成時に誘電体セラミック層を還元す

ることがなく、これにより絶縁抵抗が低下することがない。

【００１２】また、この下地導体膜表面に熱硬化性導電性樹脂膜を形成し、この熱硬化性導電性樹脂膜の表面に表面メッキ層を形成したので、下地導体膜の厚みが５～３０μｍと薄い場合であっても、メッキ液が熱硬化性導電性樹脂膜により遮断され、内部電極層を腐食させることがない。これにより、外部電極との電気的な接続が不安定となったり、また内部電極層が腐食することによるクラックやデラミネーションの発生もない。また、表面メッキ層により、熱硬化性導電性樹脂膜のハンダ濡れ性を補い、外部電極のハンダ食われを防止することができる。

【００１３】しかも、Ｎｉを主成分とする内部電極層と、Ｃｕを主成分とする下地導体膜との接合部分が、ＮｉとＣｕの合金を形成し、内部電極層と下地導体膜とが一体化し、内部電極層と外部電極とを強固に接続できる。

【００１４】さらに、本発明によれば、Ｎｉを主成分とする内部電極層と誘電体セラミック層とが交互に積層した焼成前の積層成形体が、内部電極層が酸化されない程度の低い酸素分圧中で焼成処理されて、その後、絶縁抵抗値の回復のために、高い酸素濃度雰囲気で熱処理し、Ｃｕを主成分とする下地導体膜を厚み５～３０μｍで積層焼結体の端面に形成し、下地導体膜が酸化されない程度の酸素分圧で焼成する。

【００１５】その後熱硬化性導電性樹脂膜を大気雰囲気中などで１５０℃以上の熱硬化処理を行って形成するが、外部電極を構成する熱硬化性導電性樹脂膜を大気中において低温で形成できるため、内部電極層および下地導体膜を酸化させることなく、絶縁抵抗値の劣化及び信頼性の劣化が発生しない。

【００１６】これにより、絶縁抵抗値の低下を改善しても、内部電極層と外部電極との接合信頼性は高く、しかも、内部電極層にＮｉを用いた低コストの積層セラミックコンデンサを得ることができる。

【００１７】尚、従来、特開平８－１０７０３９号公報には、内部電極層がＡｇ－Ｐｄからなり、外部電極が、内部電極層に接続されるＡｇ、Ａｇ－Ｐｄ、Ｃｕからなる下地導体膜と、この下地導体膜に形成されたＮｉ、Ｃｕメッキ膜と、このメッキ膜に形成された導電性樹脂膜と、この導電性樹脂膜の上面に形成されたＳｎ、Ｓｎ－Ｐｂのメッキ膜とから構成した積層コンデンサが開示されている。

【００１８】しかしながら、Ａｇ－Ｐｄからなる内部電極層を用いていたため、上記したようにコスト高になるという問題があったが、本願発明では、内部電極層がＮｉを主成分とするため低コストとできる。

【００１９】

【発明の実施の形態】図１は本発明の積層セラミックコンデンサを示すもので、図において、符号１は誘電体セラミック層、２はＮｉを主成分とする内部電極層、３は外部電極を示している。この積層セラミックコンデンサは、誘電体セラミック層１とＮｉを主成分とする内部電極層２とを交互に積層して積層体１０を形成し、この積層体１０の両端面に外部電極３を形成して構成されている。

【００２０】外部電極３は、積層体１０の端面側からＣｕを主成分とする下地導体膜３１、熱硬化性導電性樹脂膜３２、表面メッキ層３３とから構成されている。

【００２１】誘電体セラミック層１は、チタン酸バリウムやチタン酸バリウムに酸化イトリッウム、酸化マグネシウム、炭酸マグネシウムなどを含有する誘電体磁器であり、焼成後の１層当たりの膜厚は１０～３０μｍが望ましい。

【００２２】内部電極層２は、Ｎｉを主成分とし、概略矩形状の導体膜であり、上から第１層目、第３層目、第５層目・・・の奇数層の内部電極層２は、その一端が積層体１０の一方端面に延出しており、上から第２層目、第４層目、第６層目・・・の内部電極層２は、その一端が積層体１０の他方端面に延出している。

【００２３】Ｎｉを主成分とする内部電極層２とは、Ｎｉのみからなる場合も含まれる概念であるが、Ｎｉの酸化物を含有することがあり、さらに、例えば、Ｃｒ、Ｃｏ、Ｃｕ等の金属や化合物等が意図的に、また不純物として含まれる場合を含め、これらを総称して本発明では、Ｎｉを主成分とする内部電極層２という。

【００２４】外部電極３の一部を構成する下地導体膜３１は、焼成後の積層体１０の両端面に、Ｃｕを主成分とする導電性ペーストの塗布及び積層体１０への焼き付けによって形成されるものである。

【００２５】Ｃｕを主成分とする下地導体膜３１とは、Ｃｕのみからなるものも含まれる概念であるが、Ｃｕの酸化物を含有することがあり、さらに、例えば、Ｃｒ、Ｃｏ、Ｎｉ、Ｚｎ等の金属や化合物等が意図的に、また不純物として含まれる場合を含め、これらを総称してＣｕを主成分とする下地導体膜３１という。このＣｕを主成分とする下地導体膜３１とＮｉを主成分とする内部電極層２との接合部は、ＮｉとＣｕの合金が形成されている。

【００２６】そして、下地導体膜３１の厚みは５～３０μｍとされている。下地導体膜３１の厚みが５μｍよりも薄い場合には、内部電極層との接合が不安定となるため容量バラツキが大きくなり、３０μｍよりも厚くなると、脱バインダー処理しても電極中の炭素を完全に飛散できずに残存し、内部電極層２の焼成工程や外部電極３の形成工程で、上述のような低酸素濃度の焼成処理を行うと誘電体セラミック層１が還元され、コンデンサとしての絶縁抵抗値が低下し、信頼性不良の発生が多くなるからである。下地導体膜３１の厚みは容量、信頼性とい

う点から２０～３０μmが望ましい。

【００２７】また、熱硬化性導電性樹脂膜３２は、例えばＡｇ系（Ａｇ単体またはＡｇ合金）導体材料を含むエポキシ系などの熱硬化性樹脂で構成され、このような樹脂ペーストを下地導体膜３１表面に塗布し、大気雰囲気中で１５０～３００℃で熱処理されて形成される。

【００２８】さらに、表面メッキ層３３は、熱硬化性導電性樹脂膜３２の表面に順次形成された、例えばＮｉメッキ層、Ｓｎメッキ層、半田メッキ層などからなる積層構造であり、熱硬化性導電性樹脂膜３２の半田濡れ性を補い、また、外部電極３の半田食われを防止するものである。

【００２９】以上のように、本発明の積層セラミックコンデンサでは、先ず、内部電極層２としてＮｉを主成分とする材料を用いているため、積層セラミックコンデンサ全体として低コスト化が図れる。しかも、外部電極３を構成し、且つ内部電極層２と接続する下地導体膜３１に、Ｃｕを主成分とする材料を用いているため、下地導体膜３１を焼き付けると、内部電極層２と下地導体膜３１との接合部は、ＮｉとＣｕの合金を形成し、内部電極層２と外部電極３とが一体化し、内部電極層２と下地導体膜３１との接続を強固なものとすることができる。

【００３０】また、本発明によれば、Ｃｕを主成分とする下地導体膜３１の厚みを５～３０μmとし、従来よりも薄くしたため、脱バインダー処理において有機溶媒を完全に飛散させることができ、焼成時に誘電体セラミック層１を還元することがなく、これにより絶縁抵抗が低下することがない。

【００３１】さらにまた、その後の熱処理である外部電極３の熱硬化性導電性樹脂膜３２の形成工程では、１５０℃以上、例えば、１５０～３００℃程度の熱処理が施されるが、外部電極３の形成を大気雰囲気中で行うことができ、内部電極層２と下地導体膜３１との安定な接合が何等影響されることがない。

【００３２】また、この下地導体膜３１表面に熱硬化性導電性樹脂膜３２を形成し、この熱硬化性導電性樹脂膜３２の表面に表面メッキ層３３を形成したので、下地導体膜３１の厚みが５～３０μmと薄い場合であっても、メッキ液が熱硬化性導電性樹脂膜３２により遮断され、下地導体膜３１を介して内部電極層２を腐食させることがない。これにより、外部電極３との電気的な接続が不安定となったり、また内部電極層２が腐食することによるクラックやデラミネーションの発生もない。

【００３３】また、表面メッキ層３３により、熱硬化性導電性樹脂膜３２のハンダ濡れ性を補い、外部電極３のハンダ食われを防止することができる。

【００３４】本発明の積層セラミックコンデンサでは、内部電極層と外部電極の下地導体膜との接合が非常に安定し、セラミック焼成工程中で生じた酸素不足を解消する酸化処理を施しても両者の接合部分の酸化が進行することがなく、しかも、外部電極を構成する導電性樹脂膜を低温の大気中で形成できるため、熱履歴的な変動がなく、絶縁抵抗値の劣化及び信頼性の劣化が発生しない、安価な積層セラミックコンデンサとなる。

【００３５】次に、本発明の積層セラミックコンデンサの製法の一例を簡単に説明すると、先ず、誘電体磁器組成物に有機系粘結剤と媒体から成るバイダーを添加・撹拌してセラミック泥漿を調製した後、得られたセラミック泥漿を用いて、ドクターブレード法により誘電体セラミックグリーンシートを形成する。

【００３６】得られた誘電体セラミックグリーンシート上に、Ｎｉを主成分とする内部電極層用ペーストを用いて、内部電極層２となる導体膜を所定形状にスクリーン印刷する。その後、上述の誘電体セラミックと同一のセラミックペーストを塗布し、誘電体セラミック層１となる誘電体層を形成し、さらに、内部電極層２となる導体膜、誘電体層を交互に塗布する。このようにして、それぞれ１００回繰り返す。こうして得られた積層成形体を、所定寸法に切断してグリーンチップ（焼成前の積層体）を作製した。

【００３７】その積層成形体を脱バインダー処理、焼成を行い、続いて大気雰囲気中において再酸化処理をする。これにより、誘電体セラミック層１での絶縁抵抗値の低下を回復できる。

【００３８】次に、焼成した積層体１０の端面にＣｕを主成分とするペーストを塗布し、焼成し、下地導体膜３１を形成した後、Ａｇを含むエポキシ樹脂からなる導電性Ａｇペーストを、下地導体膜３１上に塗布し、硬化させて熱硬化性導電性樹脂膜を形成し、その後、熱硬化性導電性樹脂膜の表面に表面メッキ層を施すことにより、本発明の積層セラミックコンデンサが得られる。

【００３９】

【実施例】先ずチタン酸バリウム（$BaTiO_3$）と、このチタン酸バリウム１００重量部に対して酸化イットリウム（Y_2O_3）を１重量部、酸化マグネシウム（ＭｇＯ）を０．２重量部、炭酸マンガン（$MnCO_3$）０．１重量部、Li_2OとSiO_2とからなるガラス成分（ＬｉとＳｉのモル比が１：１）を０．５重量部含有する誘電体磁器組成物に、有機系粘結剤と媒体から成るバイダーを添加・撹拌してセラミック泥漿を調製した後、得られたセラミック泥漿を脱泡し、ドクターブレード法により厚さ７μmの誘電体セラミックグリーンシートを形成した。

【００４０】得られた誘電体セラミックグリーンシート上に、Ｎｉ粉末と、エチルセルロース、テルピネオールとからなる内部電極層用ペーストを用いてスクリーン印刷した。その後、上述の誘電体セラミックグリーンシートと同一の組成のセラミックペーストを作製塗布し、誘電体層成形体を形成し、さらに、内部電極層用ペーストとセラミックペーストの塗布を交互にそれぞれ１００回

繰り返した。こうして得られた積層成形体を、所定寸法（２１２５型）に切断してグリーンチップ（焼成前の積層成形体）を作製した。

【００４１】その積層成形体を大気中で４００℃にて脱バインダー処理を行い、その後１２５０℃（PO_2 10^{-11} ａｔｍ）で２時間焼成し、続いて大気雰囲気中８００℃で再酸化処理をした。

【００４２】次に、焼成した積層体１０の端面にロール転写法により、Ｃｕ粉末と、アクリル樹脂とからなるペーストを塗布し、酸素濃度２ｐｐｍで９００℃で焼成し、表１に示すような厚みの下地導体膜３１を形成し、Ａｇを含むエポキシ樹脂からなる導電性Ａｇペーストを、下地導体膜３１上に塗布し、２００℃、３０分で硬化させ、厚みが６０μｍの熱硬化性導電性樹脂膜を形成した。

【００４３】その後、熱硬化性導電性樹脂膜３２の表面に、厚み２μｍのＮｉメッキおよび厚み２μｍのＳｎメッキを施すことにより、本発明の積層セラミックコンデンサを作製した。得られたコンデンサの誘電体セラミック層の積層数１００層、一層当たりの厚みは５μｍであった。

【００４４】得られた積層セラミックコンデンサは、ＬＣＲメーター４２８４Ａを用い、周波数１ＫＨｚ入力信号１Ｖｒｍｓにて静電容量、誘電損失ＤＦを測定した。また、電圧１６Ｖを印加して１分間後の絶縁抵抗ＩＲを測定した。さらに、１５０℃において４０Ｖを印加する高温負荷試験を３００個行い、４０時間以内に故障した個数を測定し、信頼性不良率を算出した。また、２５０℃の半田漕に試料を浸漬しクラックの発生状態を観察した。その結果を表１に示す。

【００４５】

【表１】

試料No.	下地導体膜厚み μm	静電容量 (nF)	DF (%)	IR GΩ	信頼性不良率 %	クラック発生率%
1	5	725	3.5	22	0	0
2	10	738	2.9	22	0	0
3	20	735	3.0	22	0	0
4	30	745	2.9	22	0	0
*5	40	748	3.0	15	5	12
*6	60	745	3.9	2	28	35

＊印は本発明の範囲外の試料を示す。

【００４６】表１によれば、本発明の試料では、Ｃｕからなる下地導体膜の厚みが５～３０μｍの場合には、焼成中にカーボンにより絶縁抵抗を劣化させることはなく、絶縁抵抗が２２ＧΩ以上となり、信頼性不良率およびクラックも発生しないことが判る。Ｃｕからなる下地導体膜の厚みが３０μｍよりも厚くなると、絶縁抵抗が劣化し、信頼性不良率およびクラックの発生率も高くなることが判る。

【００４７】本発明者は、導電性樹脂膜を形成することなく、下地導体膜の表面に表面メッキ層を形成する以外は、上記と同様にして積層セラミックコンデンサを作製したところ、静電容量が７２０ｎＦ、誘電損失３．４％、絶縁抵抗ＩＲが１８ＧΩ、信頼性不良率１５％、クラックの発生率が１００％であった。

【００４８】

【発明の効果】以上のように、Ｃｕを主成分とする下地導体膜の厚みを５～３０μｍとし、従来よりも薄くしたため、脱バインダー処理において有機溶媒を完全に飛散させることができ、焼成時に誘電体セラミック層を還元することがなく、これにより絶縁抵抗が低下することがない。

【００４９】また、この下地導体膜表面に熱硬化性導電性樹脂膜を形成し、この熱硬化性導電性樹脂膜の表面に表面メッキ層を形成したので、下地導体膜の厚みが５～３０μｍと薄い場合であっても、メッキ液が熱硬化性導電性樹脂膜により遮断され、下地導体膜を介して内部電極層を腐食させることがない。

【００５０】さらに、熱硬化性導電性樹脂膜を大気雰囲気中などで１５０℃以上の熱硬化処理を行って形成できるが、外部電極を構成する熱硬化性導電性樹脂膜を大気中において低温で形成できるため、内部電極層および下地導体膜を酸化させることなく、絶縁抵抗値の劣化及び信頼性の劣化が発生しない。

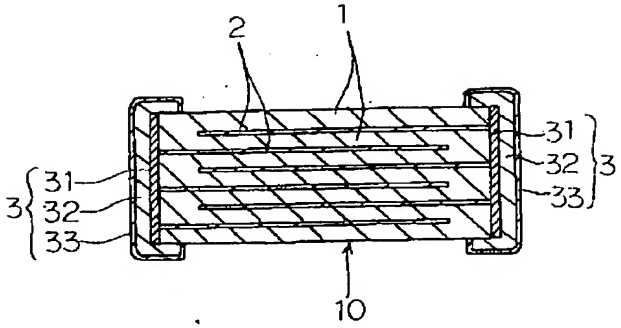
【図面の簡単な説明】

【図１】本発明の積層セラミックコンデンサの断面図である。

【符号の説明】

１・・・・誘電体セラミック層
２・・・・内部電極層
３・・・・外部電極
１０・・・・積層体
３１・・・下地導体膜
３２・・・熱硬化性導電性樹脂膜
３３・・・表面メッキ層

【図１】



* NOTICES *

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CLAIMS

[Claim(s)]
[Claim 1] The layered product which carried out the laminating of the internal electrode layer which uses a dielectric ceramic layer and nickel as a principal component by turns, the substrate of being a stacked type ceramic condenser possessing the external electrode formed in the end face of this layered product, and connecting said external electrode with said internal electrode layer -- a conductor -- with the film this substrate -- a conductor -- while constituting from thermosetting conductive resin film formed in the film front face, and a surface deposit formed in the front face of this thermosetting conductive resin film -- said substrate -- a conductor -- the stacked type ceramic condenser which the film uses Cu as a principal component, and is characterized by that thickness being 5-30 micrometers.

[Translation done.]

* NOTICES *

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] Especially this invention relates to the stacked type ceramic condenser possessing the layered product which carried out the laminating of the internal electrode layer which uses a dielectric ceramic layer and nickel as a principal component by turns, and the external electrode formed in the end face of this layered product about a stacked type ceramic condenser.
[0002]
[Description of the Prior Art] Although the Ag-Pd alloy is used as an internal electrode layer of a stacked type ceramic condenser in recent years, since it corresponds to the latest low cost-ization, base-metal ingredients, such as nickel and Cu, are used for an internal electrode layer. Since these base metal, such as nickel and Cu, is ingredients which are easy to oxidize, it is the process, for example, the formation process of an external electrode, after hitting and forming especially in the formation process of an internal electrode layer, and it is important to prevent oxidation of an internal electrode layer.
[0003] For example, the baking process of an internal electrode layer, i.e., the baking process of a laminate-molding object that the laminating of a dielectric ceramic layer and the internal electrode layer was carried out by turns, and the formation process of a subsequent external electrode were calcinated in the hypoxia concentration (10-8 - 10-12 atm) ambient atmosphere.
[0004] As an external electrode of the stacked type ceramic condenser using base-metal ingredients, such as nickel and Cu, as an internal electrode layer ingredient, to JP,8-4055,B, conventionally What consists of a copper baking electrode is indicated, and the baking electrode of the copper in such a laminating ceramic condenser 55 - 80 % of the weight of copper powder and the copper paste which serves as 5 - 20 % of the weight of glass frits from 10 - 30 % of the weight of organic vehicles were applied, and it could be burned on 800 degrees C and the conditions for 30 minutes among weak reducing atmosphere, and was formed. Such a copper baking electrode was made into the thickness of about 60-100 micrometers in order to usually prevent exfoliation etc.
[0005]
[Problem(s) to be Solved by the Invention] It remains without the ability dispersing the carbon in an electrode completely, even if it carries out debinder processing since the thickness of a copper baking electrode is as thick as 60-100 micrometers. However, with the baking process of an internal electrode layer, or the formation process of an external electrode If baking processing of the above hypoxia concentration is performed, a dielectric ceramic layer will be returned, the property of a dielectric ceramic ingredient will change, and the fatal problem that the insulation resistance value as a capacitor will fall especially will be induced.
[0006] In the stacked type ceramic condenser with which the insulation resistance value has fallen, it is possible to heat-treat in a high oxygen density ambient atmosphere, and to compensate oxygen, in order to recover an insulation resistance value. For example, when heat-treated by high oxygen tension in the baking process of the external electrode which is a heat treatment process after layered product sintering, the internal electrode layer oxidized through the external electrode, and a flow with an internal electrode layer and an external electrode could not be taken, but there was a problem of a barrack in electrostatic capacity. after all, an external electrode should be burned by low oxygen tension -- not carrying out -- it did not obtain but the improvement of the insulation resistance value

of a dielectric ceramic layer was difficult.
[0007] In order to prevent the fall of the insulation resistance of such a dielectric ceramic layer, it is possible to make a copper baking electrode thin. However, although plating processing is performed to the front face of a copper baking electrode in order to improve wettability with a pewter and to prevent a pewter foods crack of an external electrode generally This plating liquid penetrated the copper baking electrode, the internal electrode layer which uses nickel as a principal component was made to corrode, and there was a problem that the electric connection with an external electrode becomes unstable, and an internal electrode layer corroded and exfoliated and a crack and delamination occurred.
[0008] Moreover, although the copper paste could be calcinated at low temperature 800 degrees C or less in order to prevent the fall of the insulation resistance of a dielectric ceramic layer, eburnation of a copper baking electrode could not be attained in this case, but the internal electrode layer corroded after plating, and there was the same problem as the above.
[0009] It is offering the stacked type ceramic condenser which can attain the stable electric connection with the internal electrode layer and external electrode which this invention's is thought out in view of an above-mentioned technical problem, prevent the corrosion of an internal electrode layer with plating liquid while the purpose's can improve the insulation resistance of a dielectric ceramic layer, and consist of a nickel principal component.
[0010]
[Means for Solving the Problem] The layered product which carried out the laminating of the internal electrode layer to which the stacked type ceramic condenser of this invention uses a dielectric ceramic layer and nickel as a principal component by turns, the substrate of being a stacked type ceramic condenser possessing the external electrode formed in the end face of this layered product, and connecting said external electrode with said internal electrode layer -- a conductor -- with the film this substrate -- a conductor -- while constituting from thermosetting conductive resin film formed in the film front face, and a surface deposit formed in the front face of this thermosetting conductive resin film -- said substrate -- a conductor -- the film uses Cu as a principal component, and it is characterized by that thickness being 5-30 micrometers.
[0011]
[Function] the substrate which uses Cu as a principal component according to this invention -- a conductor -- membranous thickness can be set to 5-30 micrometers, it can write more thinly than before, an organic solvent can be completely dispersed in debinder processing, a dielectric ceramic layer is not returned at the time of baking, and, thereby, insulation resistance does not fall
[0012] moreover, this substrate -- a conductor -- since the thermosetting conductive resin film was formed in the film front face and the surface deposit was formed in the front face of this thermosetting conductive resin film -- a substrate -- a conductor -- even if membranous thickness is 5-30 micrometers and a thin case, plating liquid is intercepted with the thermosetting conductive resin film, and an internal electrode layer is not made to corrode The electric connection with an external electrode becomes unstable by this, and there is also no generating of the crack by an internal electrode layer corroding or delamination. Moreover, by the surface deposit, the pewter wettability of the thermosetting conductive resin film can be compensated, and a pewter foods crack of an external electrode can be prevented.
[0013] and the internal electrode layer which uses nickel as a principal component and the substrate which uses Cu as a principal component -- a conductor -- a part for a joint with the film -- the alloy of nickel and Cu -- forming -- an internal electrode layer and a substrate -- a conductor -- the film unifies and an internal electrode layer and an external electrode can be connected firmly.
[0014] According to this invention, furthermore, the laminate-molding object before baking in which the internal electrode layer which uses nickel as a principal component, and the dielectric ceramic layer carried out the laminating by turns Baking processing is carried out in the low oxygen tension which is extent to which an internal electrode layer does not oxidize. After that for recovery of an insulation resistance value the substrate which heat-treats in a high oxygen density ambient atmosphere, and uses Cu as a principal component -- a conductor -- the film -- the thickness of 5-30 micrometers -- the end face of a laminating sintered compact -- forming -- a substrate -- a conductor -- it calcinates by the oxygen tension which is extent to which the film does not oxidize.

[0015] although heat-curing processing of 150 degrees C or more is performed and the post heating hardenability conductive resin film is formed in an atmospheric-air ambient atmosphere etc., since the thermosetting conductive resin film which constitutes an external electrode can be formed at low temperature into atmospheric air -- an internal electrode layer and a substrate -- a conductor -- degradation of an insulation resistance value and degradation of ****** do not occur, without oxidizing the film.
[0016] Thereby, even if it improves the fall of an insulation resistance value, the junction dependability of an internal electrode layer and an external electrode is high, and, moreover, the stacked type ceramic condenser of the low cost which used nickel for the internal electrode layer can be obtained.
[0017] in addition, the substrate in_which of an internal electrode layer becomes JP,8-107039,A from Ag-Pd conventionally, and an external electrode consists of Ag and Ag-Pd which are connected to an internal electrode layer, and Cu -- a conductor -- the film and this substrate -- a conductor -- the multilayer capacitor constituted from nickel and Cu plating film which were formed in the film, conductive-resin film formed in this plating film, and Sn and the plating film of Sn-Pb which were formed in the top face of this conductive resin film is indicated.
[0018] However, since the internal electrode layer which consists of Ag-Pd was used, as described above, there was a problem of becoming cost quantity, but in the invention in this application, since an internal electrode layer uses nickel as a principal component, it can do with low cost.
[0019]
[Embodiment of the Invention] Drawing 1 shows the stacked type ceramic condenser of this invention, and the internal electrode layer which a sign 1 uses nickel as a dielectric ceramic layer, and 2 uses as a principal component, and 3 show the external electrode in drawing. This stacked type ceramic condenser carries out the laminating of the internal electrode layer 2 which uses the dielectric ceramic layer 1 and nickel as a principal component by turns, forms a layered product 10, forms the external electrode 3 in the both-ends side of this layered product 10, and is constituted.
[0020] the substrate in which the external electrode 3 uses Cu as a principal component from the end-face side of a layered product 10 -- a conductor -- it consists of film 31, thermosetting conductive resin film 32, and a surface deposit 33.
[0021] The dielectric ceramic layer 1 is dielectric porcelain which contains oxidation ITORIUUMU, a magnesium oxide, a magnesium carbonate, etc. in barium titanate or barium titanate, and its 10-30 micrometers are [the thickness per layer after baking] desirable.
[0022] the internal electrode layer 2 -- nickel -- a principal component -- carrying out -- an outline rectangle-like conductor -- the film -- it is -- the 1st layer from a top, the 3rd layer, and the 5th layer -- the odd-layer internal electrode layer 2 of ... the end -- a layered product 10 -- on the other hand, it has extended to the end face, and, as for the internal electrode layer 2 of ..., the 2nd layer of the end has extended from a top to the another side end face of a layered product 10 the 6th layer the 4th layer
[0023] Although it is the concept included also when consisting only of nickel in the internal electrode layer 2 which uses nickel as a principal component, the oxide of nickel may be contained, and further, including the case where metals, compounds, etc., such as Cr, Co, and Cu, are intentionally contained as an impurity, these are named generically and it is called the internal electrode layer 2 which uses nickel as a principal component by this invention.
[0024] the substrate which constitutes some external electrodes 3 -- a conductor -- the film 31 is formed in the both-ends side of the layered product 10 after baking of spreading of the conductive paste which uses Cu as a principal component, and baking to a layered product 10.
[0025] the substrate which uses Cu as a principal component -- a conductor -- the substrate which may contain the oxide of Cu, names generically these including the case where metals, compounds, etc., such as Cr, Co, nickel, and Zn, are further contained as an impurity intentionally, and uses Cu as a principal component although it is the concept in which what consists only of Cu is contained in the film 31 -- a conductor -- it is called the film 31. the substrate which uses this Cu as a principal component -- a conductor -- as for the joint with the internal electrode layer 2 which uses the film 31 and nickel as a principal component, the alloy of nickel and Cu is formed.
[0026] and a substrate -- a conductor -- thickness of the film 31 is set to 5-30 micrometers. a

substrate -- a conductor, when the thickness of the film 31 is thinner than 5 micrometers It remains without the ability dispersing the carbon in an electrode completely, even if it carries out debinder processing if capacity variation becomes large and becomes thicker than 30 micrometers, since junction in an internal electrode layer becomes unstable. With the baking process of the internal electrode layer 2, or the formation process of the external electrode 3 It is because the dielectric ceramic layer 1 will be returned, the insulation resistance value as a capacitor will fall and generating of poor dependability will increase, if baking processing of the above hypoxia concentration is performed. a substrate -- a conductor -- the thickness of the film 31 has desirable 20-30 micrometers from the point of capacity and dependability.

[0027] moreover, the thermosetting conductive resin film 32 consists of thermosetting resin, such as an epoxy system containing for example, Ag system (Ag simple substance or Ag alloy) conductor material, -- having -- such a resin paste -- a substrate -- a conductor -- it applies to film 31 front face, and is heat-treated and formed at 150-300 degrees C in an atmospheric-air ambient atmosphere.

[0028] Furthermore, the surface deposit 33 is a laminated structure which sequential formation was carried out, for example, becomes the front face of the thermosetting conductive resin film 32 from nickel deposit, Sn deposit, a solder deposit, etc., compensates the solder wettability of the thermosetting conductive resin film 32, and prevents a solder foods crack of the external electrode 3.

[0029] As mentioned above, in the stacked type ceramic condenser of this invention, since the ingredient which uses nickel as a principal component as an internal electrode layer 2 is used first, low cost-ization can be attained as the whole stacked type ceramic condenser. and the substrate which constitutes the external electrode 3 and is connected with the internal electrode layer 2 -- a conductor -- since the ingredient which uses Cu as a principal component is used for the film 31 -- a substrate -- a conductor -- if the film 31 can be burned -- the internal electrode layer 2 and a substrate -- a conductor -- the joint with the film 31 -- the alloy of nickel and Cu -- forming -- the internal electrode layer 2 and the external electrode 3 -- unifying -- the internal electrode layer 2 and a substrate -- a conductor -- connection with the film 31 can be made a firm thing.

[0030] moreover, the substrate which uses Cu as a principal component according to this invention -- a conductor -- thickness of the film 31 can be set to 5-30 micrometers, it can write more thinly than before, an organic solvent can be completely dispersed in debinder processing, the dielectric ceramic layer 1 is not returned at the time of baking, and, thereby, insulation resistance does not fall

[0031] although heat treatment of about 150 degrees C or more, for example, 150-300 degrees C, is performed further again with the formation process of the thermosetting conductive resin film 32 of the external electrode 3 which is subsequent heat treatment -- formation of the external electrode 3 -- the inside of an atmospheric-air ambient atmosphere -- it can carry out -- the internal electrode layer 2 and a substrate -- a conductor -- stable junction on the film 31 is not influenced at all

[0032] moreover, this substrate -- a conductor -- since the thermosetting conductive resin film 32 was formed in film 31 front face and the surface deposit 33 was formed in the front face of this thermosetting conductive resin film 32 -- a substrate -- a conductor -- even if the thickness of the film 31 is 5-30 micrometers and a thin case, plating liquid intercepts with the thermosetting conductive resin film 32 -- having -- a substrate -- a conductor -- the internal electrode layer 2 is not made to corrode through the film 31 The electric connection with the external electrode 3 becomes unstable by this, and there is also no generating of the crack by the internal electrode layer 2 corroding or delamination.

[0033] Moreover, by the surface deposit 33, the pewter wettability of the thermosetting conductive resin film 32 can be compensated, and a pewter foods crack of the external electrode 3 can be prevented.

[0034] the stacked type ceramic condenser of this invention -- the substrate of an internal electrode layer and an external electrode -- a conductor -- junction on a film -- very much -- be stabilize -- ceramic baking -- since the conductive resin film which both oxidation for a joint do not advance and moreover constitute an external electrode can form in low-temperature atmospheric air even if it be in process and it perform oxidation treatment which cancel the produced hypoxia, there be no heat history-fluctuation and it become the cheap laminating ceramic condenser which degradation of an insulation resistance value and degradation of ****** do not generate.

[0035] Next, if an example of the process of the stacked type ceramic condenser of this invention is

explained briefly, after adding and stirring first BAIDA which changes from an organic system binder and a medium to a dielectric porcelain constituent and preparing ceramic slurry, a dielectric ceramic green sheet is formed with a doctor blade method using the obtained ceramic slurry.
[0036] the conductor which serves as the internal electrode layer 2 on the obtained dielectric ceramic green sheet using the paste for internal electrode layers which uses nickel as a principal component -- the film is screen-stenciled in a predetermined configuration. then, the conductor which applies the same ceramic paste as an above-mentioned dielectric ceramic, forms the dielectric layer used as the dielectric ceramic layer 1, and serves as the internal electrode layer 2 further -- the film and a dielectric layer are applied by turns. Thus, it repeats 100 times, respectively. In this way, the acquired laminate-molding object was cut in the predetermined dimension, and the Green chip (layered product before baking) was produced.
[0037] Reoxidation processing is continuously performed debinder processing and baking and carried out into an atmospheric-air ambient atmosphere in the laminate-molding object. Thereby, the fall of the insulation resistance value in the dielectric ceramic layer 1 is recoverable.
[0038] next, the paste which uses Cu as a principal component at the end face of the calcinated layered product 10 -- applying -- calcinating -- a substrate -- a conductor -- the ****** Ag paste which consists of an epoxy resin containing Ag after forming the film 31 -- a substrate -- a conductor -- the stacked type ceramic condenser of this invention is obtained by applying on the film 31, making it harden, forming the thermosetting conductive resin film, and giving a surface deposit after that to the front face of the thermosetting conductive resin film.
[0039]
[Example] Barium titanate (BaTiO3) and this barium titanate 100 weight section are received first. Yttrium oxide (Y2 O3) One weight section, A magnesium oxide (MgO) The 0.2 weight section, the manganese carbonate (MnCO3) 0.1 weight section, Li2 -- O and SiO2 from -- the becoming glass component (the mole ratio of Li and Si being 1:1) to the dielectric porcelain constituent which carries out 0.5 weight section content After adding and stirring BAIDA which consists of an organic system binder and a medium and preparing ceramic slurry, degassing of the obtained ceramic slurry was carried out, and the dielectric ceramic green sheet with a thickness of 7 micrometers was formed with the doctor blade method.
[0040] On the obtained dielectric ceramic green sheet, it screen-stenciled using the paste for internal electrode layers which consists of nickel powder, and ethyl cellulose and a terpineol. Then, production spreading of the ceramic paste of the same presentation as an above-mentioned dielectric ceramic green sheet was carried out, the dielectric layer Plastic solid was formed, and spreading of the paste for internal electrode layers and a ceramic paste was repeated further 100 times by turns, respectively. In this way, the acquired laminate-molding object was cut in the predetermined dimension (2125 molds), and the Green chip (laminate-molding object before baking) was produced.

[0041] Debinder processing was performed at 400 degrees C in atmospheric air, the laminate-molding object was calcinated at 1250 degrees C (PO2 10-11 atm) after that for 2 hours, and reoxidation processing was continuously carried out at 800 degrees C among the atmospheric-air ambient atmosphere.
[0042] next, the substrate of thickness as applied the paste which consists of Cu powder and acrylic resin to the end face of the calcinated layered product 10, calcinated at 900 degrees C by 2 ppm of oxygen densities to it and shown in Table 1 with a roll replica method at it -- a conductor -- the ****** Ag paste which consists of an epoxy resin which forms the film 31 and contains Ag -- a substrate -- a conductor -- applied on the film 31, made it harden in 200 degrees C and 30 minutes, and the thermosetting conductive-resin film whose thickness is 60 micrometers formed.
[0043] Then, the stacked type ceramic condenser of this invention was produced by performing nickel plating with a thickness of 2 micrometers and Sn plating with a thickness of 2 micrometers to the front face of the thermosetting conductive resin film 32. The thickness of the 100 layers of the laminating number of the dielectric ceramic layers of the obtained capacitor and much more a hit was 5 micrometers.
[0044] The obtained stacked type ceramic condenser measured electrostatic capacity and dielectric loss DF in frequency input signal [of 1kHz] 1Vrms using LCR meter 4284A. Moreover, electrical-

potential-difference 16V were impressed and the insulation resistance IR of 1 minute after was measured. Furthermore, 300 elevated-temperature load tests which impress 40V in 150 degrees C were performed, the number which broke down within 40 hours was measured, and the dependability percent defective was computed. Moreover, the sample was immersed in the 250-degree C Handa **, and the generating condition of a crack was observed. The result is shown in Table 1.

[0045]

[Table 1]

試料 No.	下地導体膜 厚み μm	静電容量 (nF)	DF (%)	IR GΩ	信頼性不良率 %	クラック発生率%
1	5	725	3.5	22	0	0
2	10	738	2.9	22	0	0
3	20	735	3.0	22	0	0
4	30	745	2.9	22	0	0
*5	40	748	3.0	15	5	12
*6	60	745	3.9	2	28	35

*印は本発明の範囲外の試料を示す。

[0046] the substrate which consists of Cu by the sample of this invention according to Table 1 -- a conductor -- when membranous thickness is 5-30 micrometers, insulation resistance is not degraded with carbon during baking, insulation resistance becomes more than 22Gohm, and it turns out that a dependability percent defective and a crack are not generated, either. the substrate which consists of Cu -- a conductor -- when membranous thickness becomes thicker than 30 micrometers, insulation resistance deteriorates and it turns out that a dependability percent defective and the incidence rate of a crack also become high.

[0047] without this invention person forms the conductive resin film -- a substrate -- a conductor -- except forming a surface deposit on the surface of the film, when the stacked type ceramic condenser was produced like the above, for electrostatic capacity, 720nF(s), 3.4% of dielectric loss, and insulation resistance IR were [18Gohm, 15% of dependability percent defectives, and the incidence rate of a crack] 100%.

[0048]

[Effect of the Invention] as mentioned above, the substrate which uses Cu as a principal component -- a conductor -- membranous thickness can be set to 5-30 micrometers, it can write more thinly than before, an organic solvent can be completely dispersed in debinder processing, a dielectric ceramic layer is not returned at the time of baking, and, thereby, insulation resistance does not fall

[0049] moreover, this substrate -- a conductor -- since the thermosetting conductive resin film was formed in the film front face and the surface deposit was formed in the front face of this thermosetting conductive resin film -- a substrate -- a conductor -- even if membranous thickness is 5-30 micrometers and a thin case, plating liquid intercepts with the thermosetting conductive resin film -- having -- a substrate -- a conductor -- an internal electrode layer is not made to corrode through the film

[0050] although heat-curing processing of 150 degrees C or more is performed and the thermosetting conductive resin film can be formed in an atmospheric-air ambient atmosphere etc., since [furthermore,] the thermosetting conductive resin film which constitutes an external electrode can be formed at low temperature into atmospheric air -- an internal electrode layer and a substrate -- a conductor -- degradation of an insulation resistance value and degradation of ****** do not occur, without oxidizing the film.

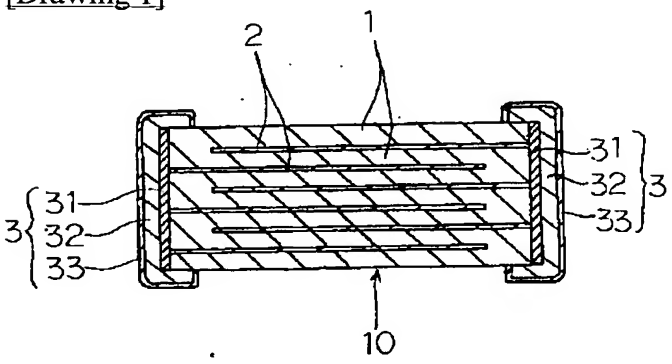
[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]



[Translation done.]